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Electronic Supplementary Information

A bifunctional metal-organic framework featuring the combination of open metal sites and Lewis basic sites for selective gas adsorption and heterogeneous cascade catalysis

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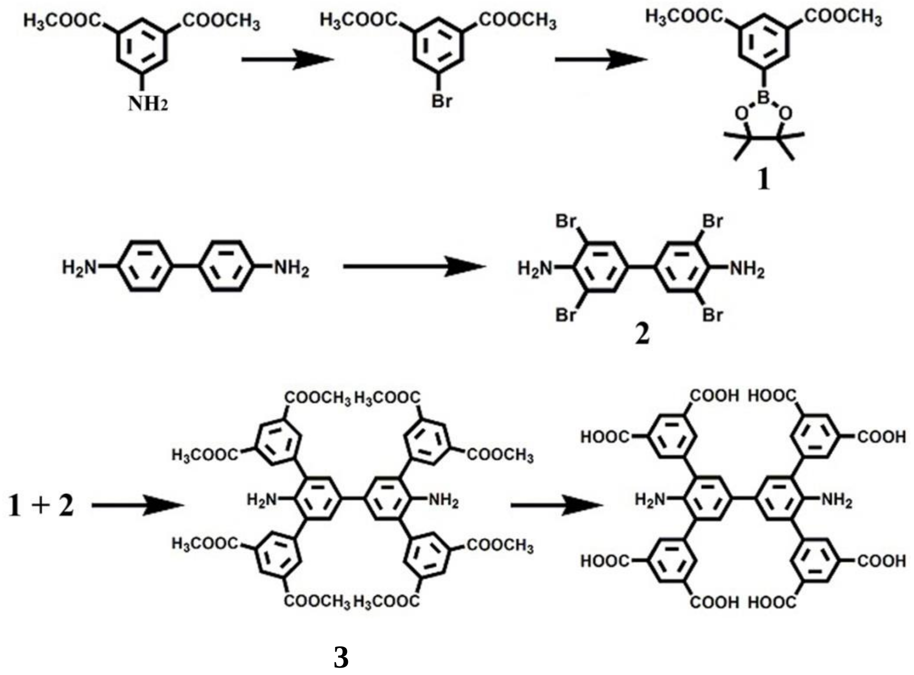
Content

S1. Synthesis of the ligand H_8TBCB

Ligand H_8TBCB was synthesized as follows:



Scheme S1. Synthetic route to the ligand H_8TBCB.

Benzene-1,3,5-tris(3’,5’-benzenedicarboxylic acid dimethyl ester) (**1**) [1] and 4,4-diaminobiphenyl-3,3’,5,5’-tetrabromide (**2**) [2] were prepared and assigned by literature procedures.

Compound **1** (1.6 g, 5.0 mmol), compound **2** (0.50 g, 1.0 mmol) and K_2CO_3 (0.69 g, 5.0 mmol) were added to a three necked-flask with toluene-ethanol-water (30 ml, 15 ml, 15 ml). After the mixture was degassed using N_2 for 15 min, $Pd(PPh_3)_4$ (0.058 g, 0.05 mmol) was added to the stirred reaction mixture. The solution was stirred under nitrogen atmosphere for 72 h with reflux. The product was extracted using $CHCl_3$ (30 ml × 3), washed with brine (30 ml), and dried with anhydrous $MgSO_4$. The filtered solution was eliminated under reduced pressure. The residue was purified using column chromatography with silica gel (CH_2Cl_2/EtOAc=1/1, v/v) to obtain compound **3** of 0.552 g (yield: 58%). ^1H NMR (300 Hz, $CDCl_3$, ppm): 8.70 (t, 3.9 H), 8.40 (d, 8.0 H), 7.37 (s, 4.0 H), 4.42 (m, 3.9 H), 3.96 (s, 24.1 H).

Compound **3** (0.5 g, 0.5 mmol) and NaOH (1.0 g, 25 mmol) were added to a flask with a mixed solvent of THF-methanol-water (20 ml, 10 ml, 10 ml). The mixture was stirred under reflux overnight. After cooling to room temperature slowly, THF and MeOH were removed under vacuum. Dilute HCl solution (2 M) was slowly added to the resultant solution until the value of pH was about 2.0-3.0. Yellow precipitation was filtered and washed with H_2O and MeOH, and dried to obtain H_8TBCB of 0.39 g (yield: 94%). Selected FT-IR data (KBr pellet, cm^{-1}): 2966 (br), 2609 (s), 1705 (s), 1595 (s), 1452 (s), 1257 (s), 1203 (s), 1113 (s), 918 (s), 874 (s), 802 (s), 764 (s), 663 (s), 540 (s). ^{1}HNMR (300 Hz, DMSO-d_6, ppm): 13.25 (s, 8.0 H), 8.45 (s, 4.0 H), 8.24 (s, 8.1 H), 7.45 (s, 3.9 H), 4.26 (s, 4.0 H).

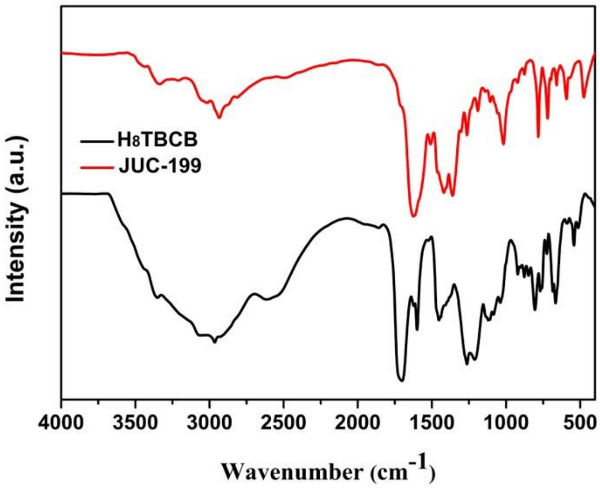


Fig. S1. FT-IR spectra of H_8TBCB (black) and JUC-199 (red). The characteristic peak of carbonyl asymmetric stretching band (C=O) of –COOH at 1705 cm^{-1} was only found in the black curve, implying that all carboxyl groups of ligand are deprotonated.

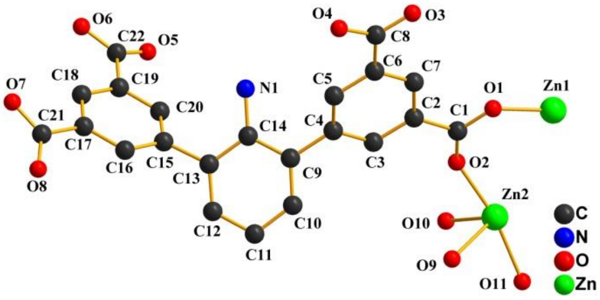


Fig. S2. The asymmetric unit of JUC-199.

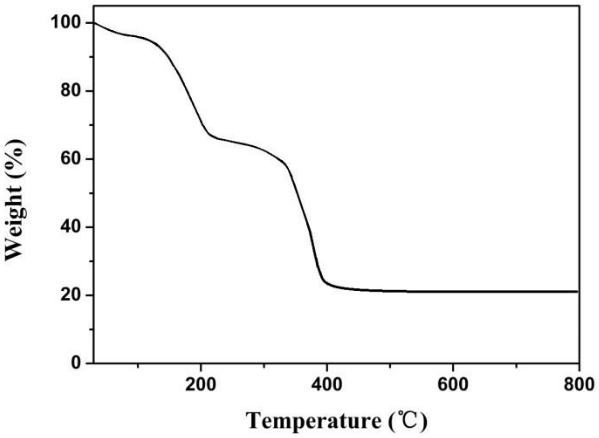


Fig. S3. The TGA curve of the as-synthesized JUC-199.

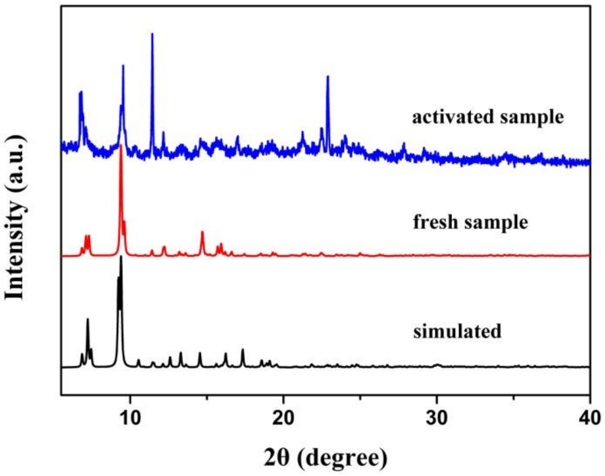


Fig. S4. The PXRD patterns of simulated (black), as-synthesized sample (red) and activated sample (blue).

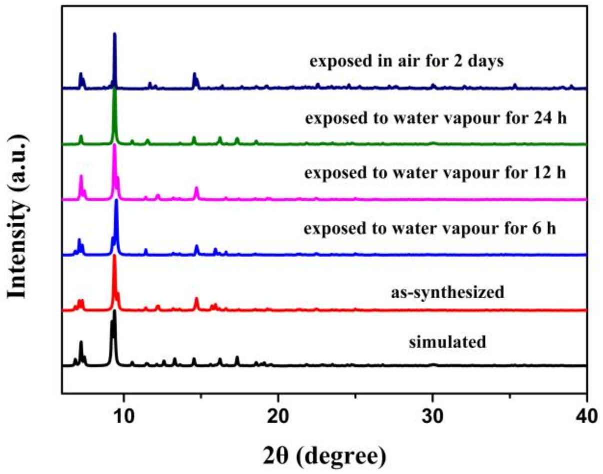


Fig. S5. The PXRD patterns of JUC-199 after exposure to water vapour for 6, 12 and 24 hours, and in air for 2 days, respectively.

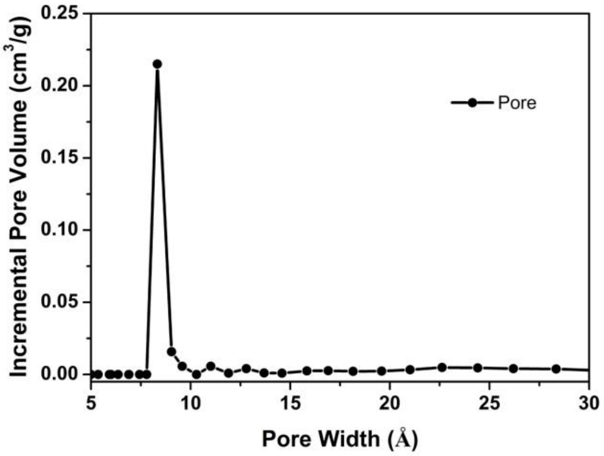


Fig. S6. The pore size distribution was calculated by the Horvath-Kawazoe method.

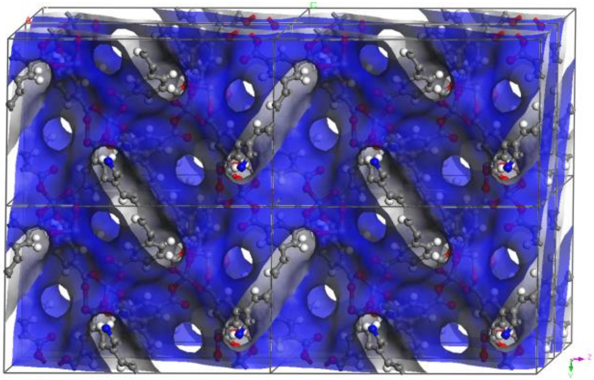


Fig. S7. Grand canonical Monte Carlo (GCMC) simulations were performed to evaluate the surface area of desolvated JUC-199 in a 2×2×2 cell in Sorption Module of Materials Studio.

S2. Gas sorption and IAST calculations

The adsorption isotherms for CO_2, N_2, CH_4, C_2H_4 and C_2H_6 (273 K and 298 K) were first converted to absolute loadings according to Peng-Robinson Equation. In order to perform the IAST calculation, the single-component gas absorption isotherms was fitted by the dual-site Langmuir-Freundlich (DSLF) adsorption model, which was adopted to correlate the pure-component equilibrium data and further to evaluate the adsorption of binary gas mixtures. The DSLF model is described as: $N_0\ (f) = N_1 k_1 f/(1+\mathrm{k}_1 f) + N_2 k_2 f/(1+\mathrm{k}_2 f)$ (1)

where f is the fugacity of bulk gas at equilibrium with adsorbed phase, N_i is the model parameter of the maximum adsorption amount at the site i (i = 1 or 2) and k_i is the affinity constant.

Based on the above model parameters of pure gas adsorption, we used the IAST model, which was proposed by Myer and Prausnitz in 1965 to predict the multi-component adsorption.

Table S1. Summary of the parameters of the experimentally measured gas adsorption isotherms of **JUC-199** at 298 K fitted with dual-site Langmuir-Freundlich adsorption model-based IAST theory.

	CO_2	N_2	CH_4	C_2H_4	C_2H_6
R^2	1	0.99995	0.99999	0.99998	0.99988
a_1	0.47737	0.60191	0.00348	0.60398	1.38295
a_2	2.93112	1.42711	1.57162	1.59738	0.44072
b_1	0.06869	3.36889E-4	1.20638	0.78521	0.05635
b_2	0.00855	0.00105	0.00463	0.03795	0.51493
c_1	1	1	0.98075	1	1
c_2	1	1	0.99968	1	1

S3. Calculations of the isosteric heats of gas adsorption (Q_{st})

A virial-type expression comprising the temperature-independent parameters a_i and b_j was employed to calculate the enthalpies of adsorption for CO_2, N_2, CH_4, C_2H_4 and C_2H_6 (273 and 298 K). In each case, the data were fitted using the equation:

$$ln^P = ln^N + 1/T \sum_{i-0}^{m} a_i N^i + \sum_{j-0}^{n} b_j \, N^j$$

Here, P is the pressure expressed in Torr, N is the amount adsorbed in mg g^{-1}, T is the temperature in K, a_i and b_j are virial coefficients, m, n represent the number of coefficients required to adequately describe the isotherms (m and n were gradually increased until the contribution of extra added a and b coefficients was deemed to be statistically insignificant towards the overall fit, and the average value of the squared deviations from the experimental values was minimized). The values of the virial coefficients a_0 through a_m were then used to calculate the isosteric heat of adsorption using the following expression.

$$Q_{st} = -R \sum_{i-0}^{m} a_i \, N^i$$

Q_{st} is the coverage-dependent isosteric heat of adsorption and R is the universal gas constant. The heats of gas sorption for JUC-199 in this manuscript are determined by using the sorption data measured in the pressure range from 0-1 bar, which is fitted by the virial-equation very well.

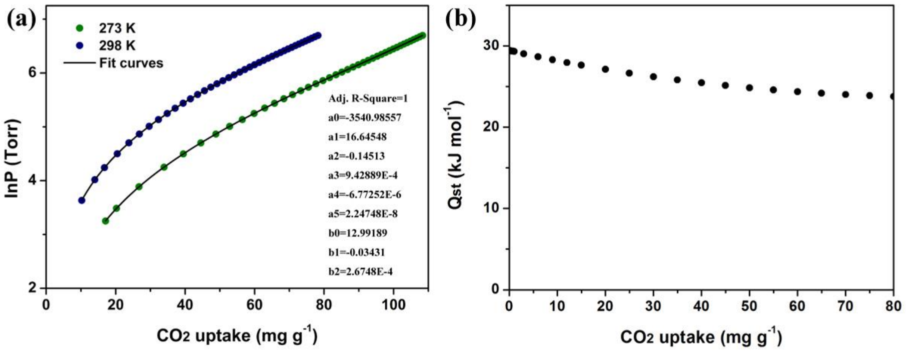


Fig. S8. (a) Nonlinear curves fitting of CO_2 for JUC-199 at 273 K and 298 K; (b) Isosteric heat of CO_2 for JUC-199.

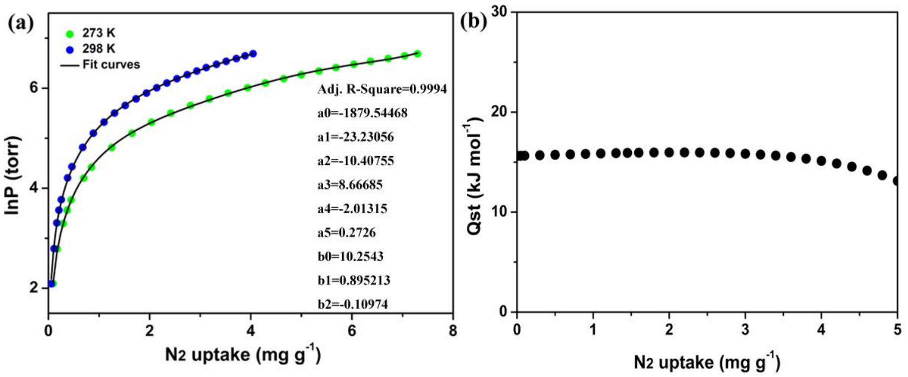


Fig. S9. (a) Nonlinear curves fitting of N_2 for JUC-199 at 273 K and 298 K; (b) Isosteric heat of N_2 for JUC-199.

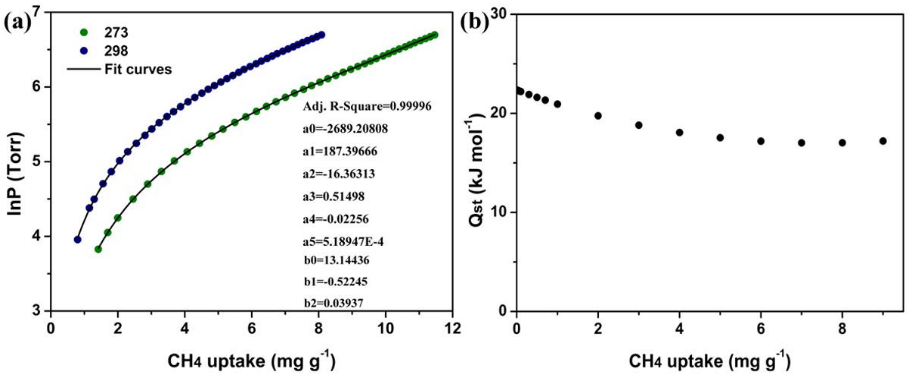


Fig. S10. (a) Nonlinear curves fitting of CH_4 for JUC-199 at 273 K and 298 K; (b) Isosteric heat of CH_4 for JUC-199.

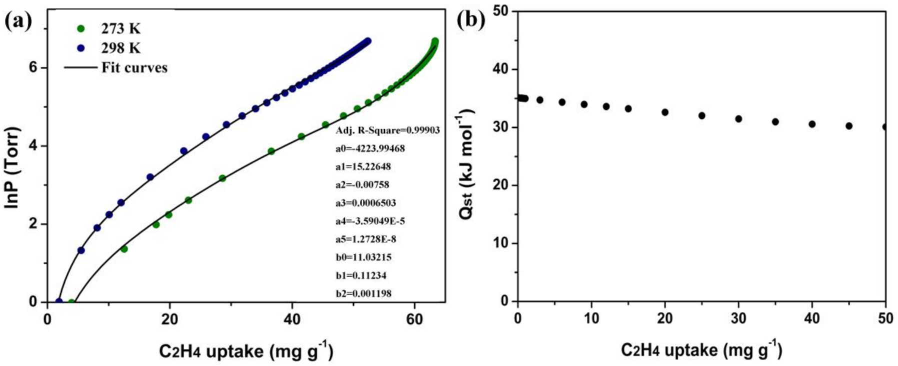


Fig. S11. (a) Nonlinear curves fitting of C_2H_4 for JUC-199 at 273 K and 298 K; (b) Isosteric heat of C_2H_4 for JUC-199.

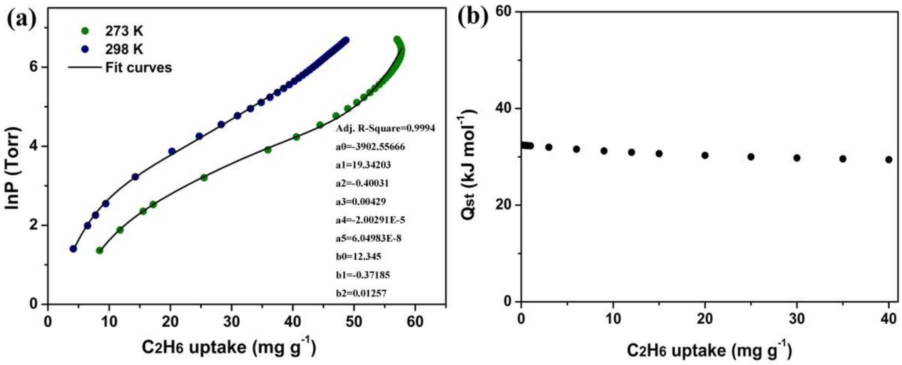


Fig. S12. (a) Nonlinear curves fitting of C_2H_6 for JUC-199 at 273 K and 298 K; (b) Isosteric heat of C_2H_6 for JUC-199.

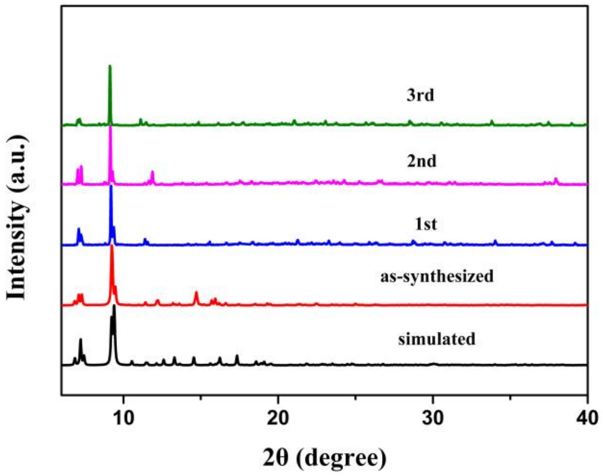


Fig. S13. The PXRD patterns of reused samples.

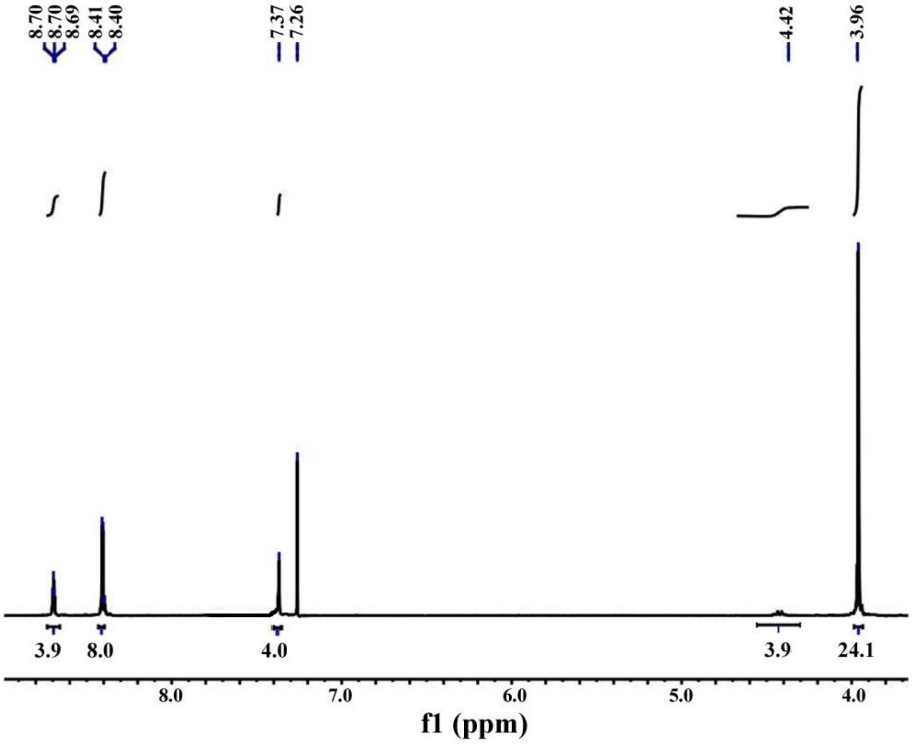


Fig. S14. The ^{1}H NMR spectra of compound **3** in $CDCl_3$.

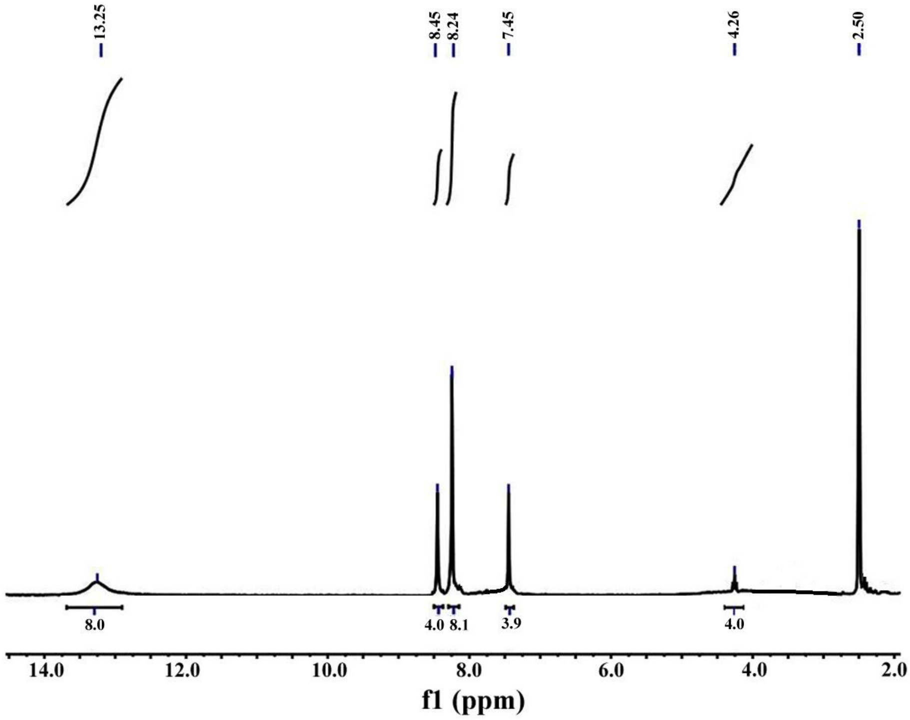


Fig. S15. The ^{1}H NMR spectra of H_8TBCB in d_6-DMSO.

Table S2. Selected bond lengths (Å) and angles (deg) for JUC-199.

JUC-199			
O(1)-Zn(1)	1.9060(18)	O(2)-Zn(2)	2.0436(19)
O(3)-Zn(2)#2	2.101(2)	O(4)-Zn(1)#2	1.923(2)
O(5)-Zn(2)#3	2.068(2)	O(6)-Zn(1)#3	1.9478(19)
O(7)-Zn(1)#4	1.9320(17)	O(9)-Zn(2)	2.141(2)
O(10)-Zn(2)	2.203(3)	O(11)-Zn(2)	2.139(3)
Zn(1)-O(4)#5	1.923(2)	Zn(1)-O(7)#6	1.9321(17)
Zn(1)-O(6)#7	1.9478(19)	Zn(2)-O(5)#7	2.068(2)
Zn(2)-O(3)#5	2.101(2)		
O(1)-Zn(1)-O(4)#5	122.98(10)	O(1)-Zn(1)-O(7)#6	106.50(9)
O(4)#5-Zn(1)-O(7)#6	105.46(9)	O(1)-Zn(1)-O(6)#7	113.12(10)
O(4)#5-Zn(1)-O(6)#7	105.26(10)	O(7)#6-Zn(1)-O(6)#7	101.16(9)
O(2)-Zn(2)-O(5)#7	98.84(9)	O(2)-Zn(2)-O(3)#5	94.61(8)
O(5)#7-Zn(2)-O(3)#5	91.36(9)	O(5)#7-Zn(2)-O(11)	89.08(9)
O(3)#5-Zn(2)-O(11)	93.11(9)	O(2)-Zn(2)-O(9)	87.23(9)
O(3)#5-Zn(2)-O(9)	93.33(10)	O(11)-Zn(2)-O(9)	84.22(10)
O(2)-Zn(2)-O(10)	85.50(13)	O(5)#7-Zn(2)-O(10)	83.17(14)
O(11)-Zn(2)-O(10)	87.60(13)	O(9)-Zn(2)-O(10)	92.19(15)

Symmetry transformations used to generate equivalent atoms:

#1 –x, -y+1, -z #2 –x+1, y-1/2, -z+1/2 #3 -x, y-1/2, -z+1/2 #4 x-1, -y+1/2, z-1/2 #5 –x+1, y+1/2, -z+1/2 #6 x+1, -y+1/2, z+1/2 #7 –x, y+1/2, -z+1/2

S4. References

[1] Z. Chen, S. Xiang, T. Liao, Y. Yang, Y.-S. Chen, Y. Zhou, D. Zhao and B. Chen, *Cryst. Growth & Des.*, 2010, **10**, 2775.

[2] P. Wehrmann and S. Mecking, *Organometallics*, 2008, **27**, 1399.